EXWC Demonstration Projects for PFAS Characterization and Treatment
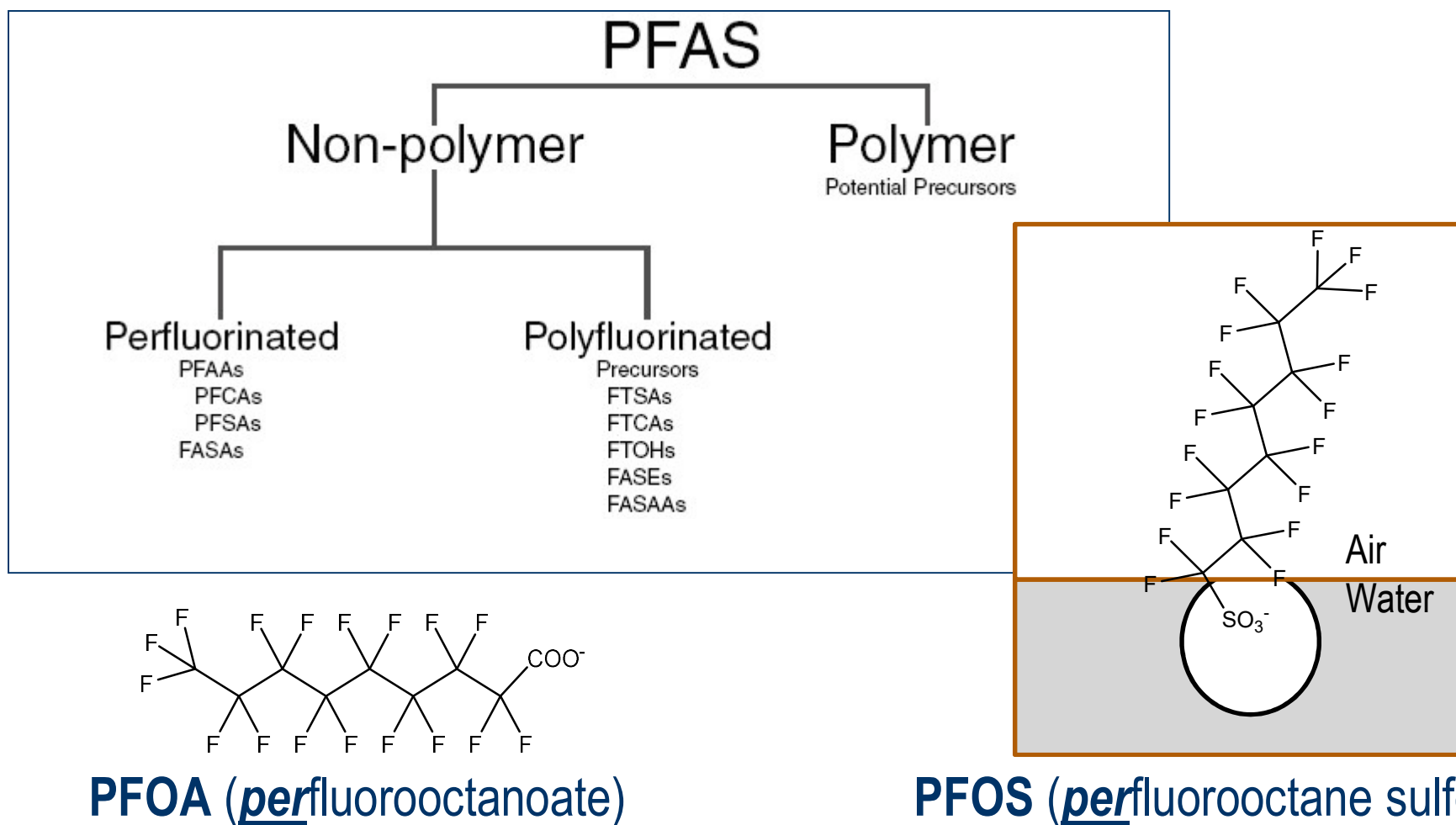
Presented By:

John Kornuc

Naval Facilities Engineering Command (NAVFAC)

Engineering and Expeditionary Warfare Center (EXWC)

Per- and polyfluoroalkyl substances (PFASs)

PFOA (*per*fluorooctanoate)

PFOS (*per*fluorooctane sulfonate)

PFAS Structure
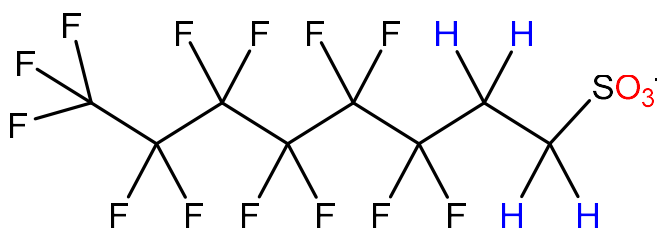## Perfluorinated vs. Polyfluorinated

- **Perfluorinated**
  - *all* carbons bonded only to F
  - Includes PFOS, PFOA (EPA LHA), and PFBS (RfD)
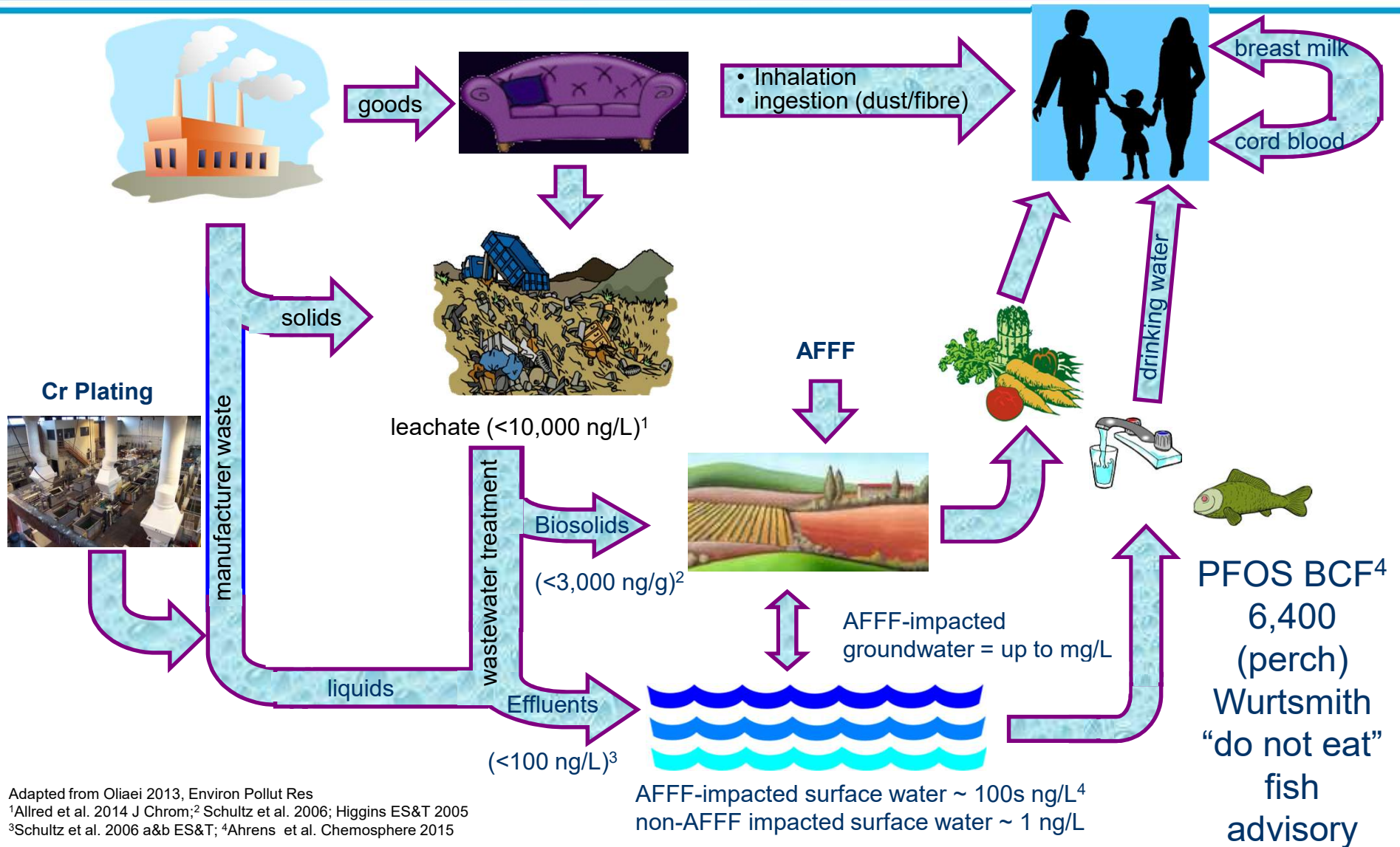 - no degradation in environment

- **Polyfluorinated**
  - *not all* carbons in chain bonded to F
  - CH_2 – linkages create "weakness" in molecule, susceptible to biodegradation, abiotic processes (e.g., oxidation)

6:2 FTSA (fluorotelomer sulfonate) - Polyfluorinated

PFAS Exposure
Sources & Exposure Pathways

- Inhalation
- ingestion (dust/fibre)

breast milk

cord blood

drinking water

goods

solids

Cr Plating

manufacturer waste

wastewater treatment

leachate (<10,000 ng/L)[1]

AFFF

Biosolids

(<3,000 ng/g)[2]

liquids

Effluents

(<100 ng/L)[3]

AFFF-impacted groundwater = up to mg/L

PFOS BCF[4] 6,400 (perch) Wurtsmith "do not eat" fish advisory

AFFF-impacted surface water ~ 100s ng/L[4]
non-AFFF impacted surface water ~ 1 ng/L

Adapted from Oliaei 2013, Environ Pollut Res
[1]Allred et al. 2014 J Chrom;[2] Schultz et al. 2006; Higgins ES&T 2005
[3]Schultz et al. 2006 a&b ES&T; [4]Ahrens et al. Chemosphere 2015
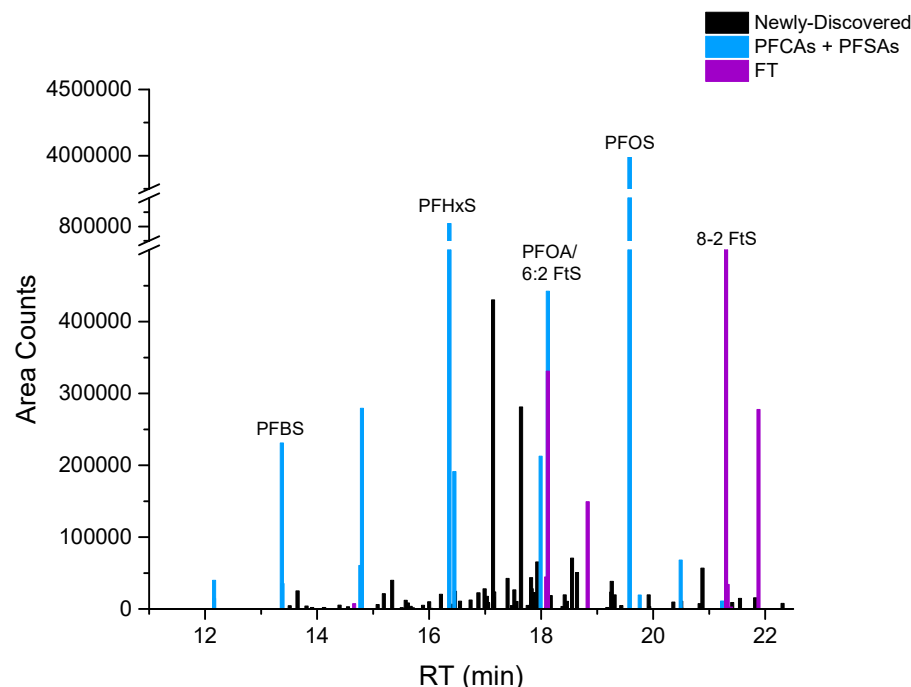
PFAS Exposure
Health Advisory Levels

- **Many PFASs detected in human blood**

- **Based on 3M (industrially-exposed) workers**
  - **PFOA 2.3 yrs to 3.5 – 3.8 yrs**
  - **PFOS 4.8 - 5.4 yrs**
  - **PFHxS 7.3 – 8.5 yrs (longest reported half life of any PFAS); reformulated AFFF based on C6 chemistry**
  - **PFBS 26 days**

- **Animal study (rats, mice) half lives much shorter (days, weeks) leading to uncertainty when extrapolating results to humans**

- **Uncertainty factors and other factors, lifetime exposure (70 years) results in low Lifetime Health Advisory (LHA)**
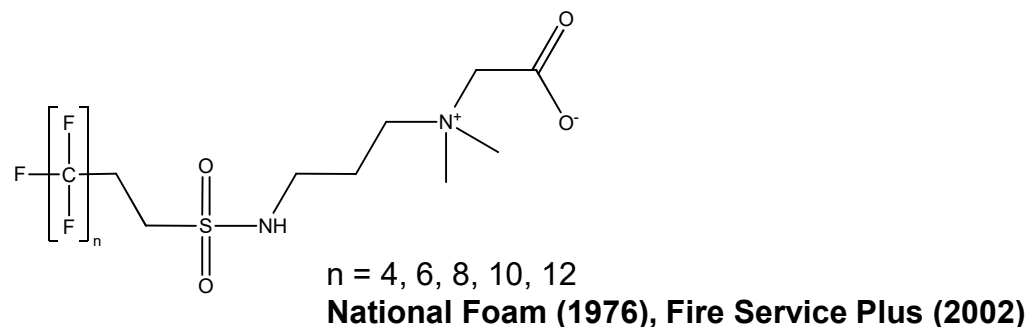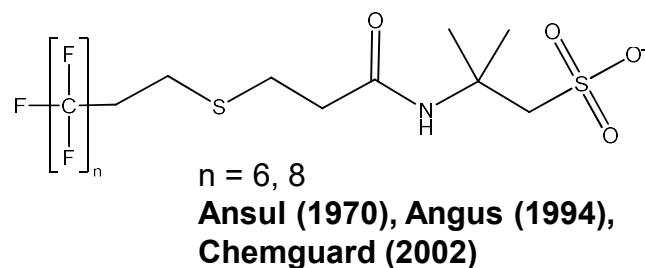
Many PFAS Compounds

- **Estimates of the total number of PFAS compounds range into the thousands**

- **PFAS associated with AFFF formulations used by DoD (QPL list products), numbers about 400 - including transformation products and intermediates after release**

- **EPA 537 & QSM 5.1 Table B-15 Methods - 14 compounds**

- **TOP Assay (precursors) and the high res MS library converging**

- **Eventually regulated as a group? (PCBs, Dioxins, PAHs)**

LC-MS/MS Relative Concentrations of PFASs

Fluorotelomer-Based AFFFs

n = 6, 8
Ansul (1970), Angus (1994),
Chemguard (2002)

n = 4, 6, 8, 10, 12
National Foam (1976), Fire Service Plus (2002)

- Add to total mass of F

- None on Method 537

- Potential to degrade to 6:2 & 8:2 fluorotelomer sulfonates & PFCAs

n = 6, 8
Angus (1994)

n = 6, 8
National Foam (1976), Fire Service Plus (2002)

- 6:2 & 8:2 fluorotelomer sulfonates not major components in AFFF

- Cations and zwitterions may sorb to source zone soils and slowly degrade to PFCAs and other mobile species

n = 5, 7, 9
Buckeye (2002)

n = 5, 7, 9
Buckeye (2002)
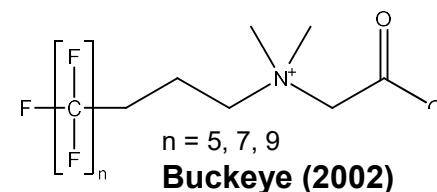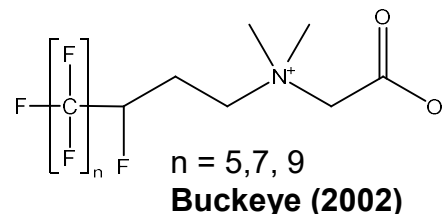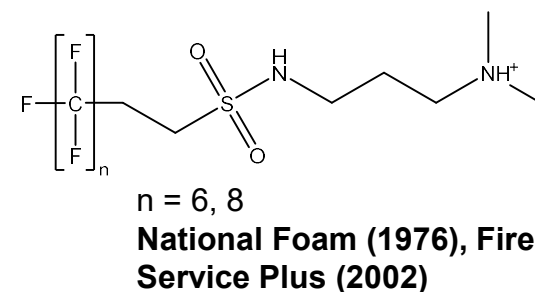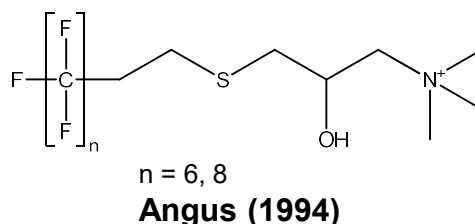
PFOS/PFOA Transport Phys/Chem Properties

- **PFOS & PFOA disassociate in water since are strong acids (pKa < 1)**
  - **Ionized (deprotonated) forms:**
    - perfluorooctano*ate* ($-COO^-$) & perfluorooctane sulfon*ate* ($-SO_3^-$)
  - **Negatively-charged anions at environmental & physiological pHs (4-10)**
  - **Low vapor pressure and Henry's Law so cannot be air-stripped (caution when disposing of 'treated' water from air stripper systems**
  - **Moderate Koc – transport slowed by natural and co-contaminant organics**
  - **Readily transported; soluble**

PFAS Transport
Site Considerations – Sources

AFFF product used – AFFF Firefighter Training Areas typically used variety of AFFF products over service life

- **3M products** (electrofluorination process)

    - high concentrations of PFOS

    - low PFOA (though test samples only date back to 80s, possible that early versions contained more PFOA)

    - perfluoroalkyl compounds

    - "messy" chemistry produced linear & branched forms, and even & odd carbon chain lengths, anions, zwitterions & cations

- **All other products/manufacturers** (fluorotelomerization processes)

    - polyfluoroalkyl compounds

        - can transform to "dead-end" products like perfluoroalkyl acids including PFOA

    - wide variety of compounds in many classes

        - 57 classes total (including perfluoroalkyls), about 400 compounds associated with AFFF and impacted sites

PFAS Transport
Site Considerations – Sources

Relative strength of sources

AFFF >>> Cr plating bath mist suppressant > landfill leachate > wastewater treatment effluent

- FFTAs were unlined earthen pits until the 80s and 90s, used repeatedly; various AFFFs used (3M early 70s, then a mix of electrofluorination and telomerization-based products)

Mass/volume of release

- FFTAs were used repeatedly (weekly training typical)
- Crash sites where AFFF was used; mix of products
- Firefighting equipment testing and cleanout/spills can result in many small source areas throughout installation
- AFFF storage/transfer areas
- Wastewater treatment receiving AFFF; effluent and biosolids can be significant source
- Low concentration sources can be high volume and long periods

PFAS Transport
Site Considerations – Sources

General PFAS structural consideration wrt transport/sorption

- PFOS and PFOA are both always anionic, therefore move relatively freely

- PFOS and PFOA are also subject to sorption on organics due to 8-carbon C-F tail (PFOA only has 7 C-F$_2$ moieties, so less hydrophobic and carboxylate more ionic)

- Smaller PFASs with shorter C-F tails are less hydrophobic, not retarded by organics (TOC) as much, therefore move faster (PFBA, a C4, found near toe of plumes); Van der Waals interactions with substrate

- Branched structures (3M) more "ball-like", less hydrophobic character to bind with organics, move slightly faster than linear counterpart

- Cationic head groups (positively charged) can sorb to negatively charged minerals (e.g. clay minerals)

- Zwitterionic compounds can also sorb to soil, or move when pH changes

- Cationic and zwitterionic species can act as long-term sources of PFASs by slowly desorbing/transforming, such as when exposed to oxic conditions

PFAS Transport
Site Considerations – Geochemistry and Hydrology

Site conditions

- Low k/permeability zones (silts/clays) can back-diffuse PFASs

- Organic soils can sorb and retard movement especially longer chain length and neutral or less polar head groups

- Clays, silts can bind cationic and zwitterionic compounds through electrostatic interaction

- Large groundwater gradients can result in long plumes (e.g. plumes in Australia about 7 km long)

- Water table fluctuations create larger smear zones

- Elevated salinity/seawater increases sorption of PFAAs (seawater wedges stop advancement of plume); divalent cations bridge binding

Characterization of PFAS Source Areas, Plumes (ESTCP ER-201633) and Structure-Activity Relationships (NESDI 527)

Objectives

- Determine the nature and extent of PFAS source areas using high-resolution sampling and advanced analytical techniques

- Differentiate AFFF and non-AFFF sources

- Identify site-specific geochemical and hydrologic factors that affect PFAS transport, including natural attenuation/transformation

- Characterize PFAS composition along plume

- Demonstrate a novel screening method for total fluorine (PIGE)

- Compare LC-MS/MS to TOP Assay and PIGE

- PFAS structure/charge on transport & uptake

- Develop guidance for RPMs

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University of Notre Dame, South Bend, IN

PFAS Characterization NAS Jacksonville FT-02

PFAS Characterization NAS Jacksonville FT-02

Naval Air Station (NAS) Jacksonville, FL, Fire-training area FT-02

- In use 1970-1996

- 120' diameter unlined pit

- TPH, BTEX in pit previously treated by low-temp thermal desorption (treated soil backfilled into pit), and air sparging

- GW 1-10 ft. bgs, flow N-NE (varies to S)

- High PFOS concentration in water (1.1 mg/L)

- Large number of PFAS compounds; cationic species present

Wastewater Treatment Plant

Shallow Monitoring Well	◎
Deep Monitoring Well	◉

Site Description: FFTF and WWTP NAS Jacksonville
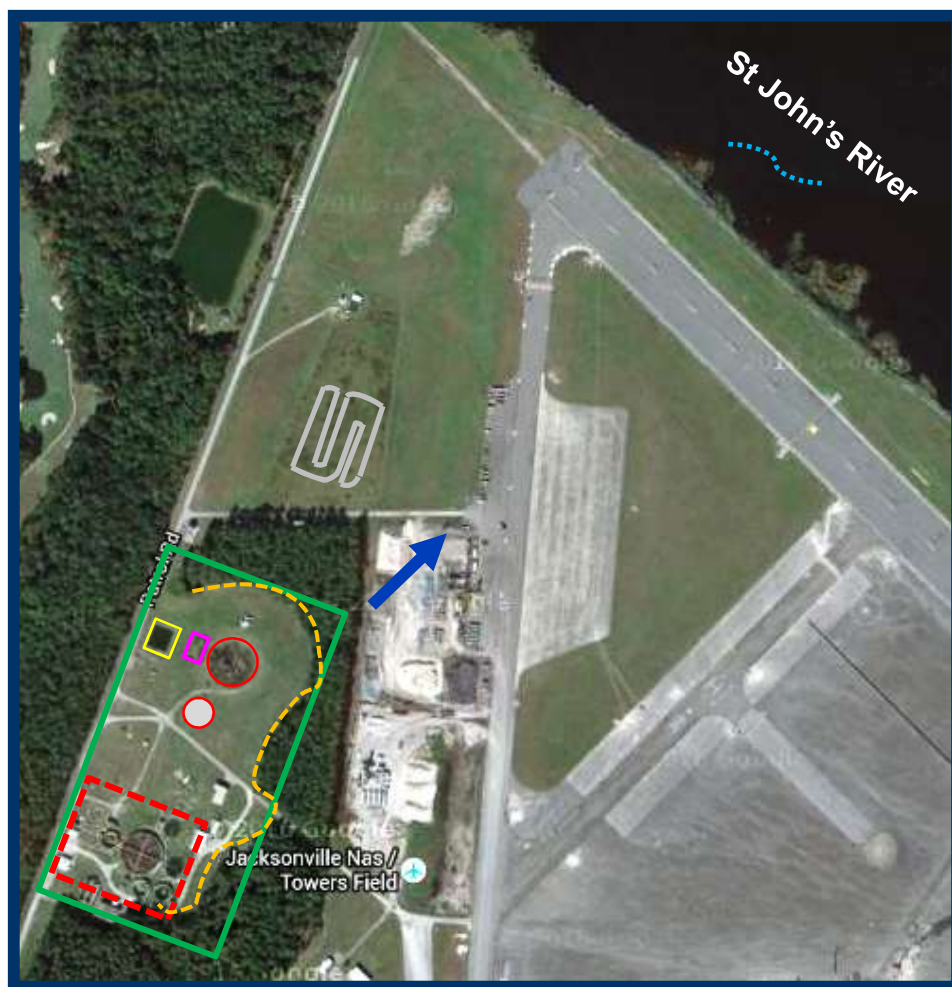
⬭ (red/gray)	Former Training Area – In use 1968-91
◯ (red)	Newer Fire Training Area
▢ (yellow)	Pond/Pump Station
⬚ (red dashed)	Waste Water Treatment Plant
(gray)	Unlined Polishing Pond
▱ (magenta)	OW Separator
(blue dotted)	St. John's River
(orange dotted)	Tree Line
➚ (blue arrow)	GW: Primarily N/NE

PFAS Characterization
2-Tiered Sampling Approach

Sampling Overview: Soil

Groundwater flow direction

● Tier 1 Soil Sample Transects (10 depths each)

✖ Tier 2 Soil Sample Locations (4 depths each)
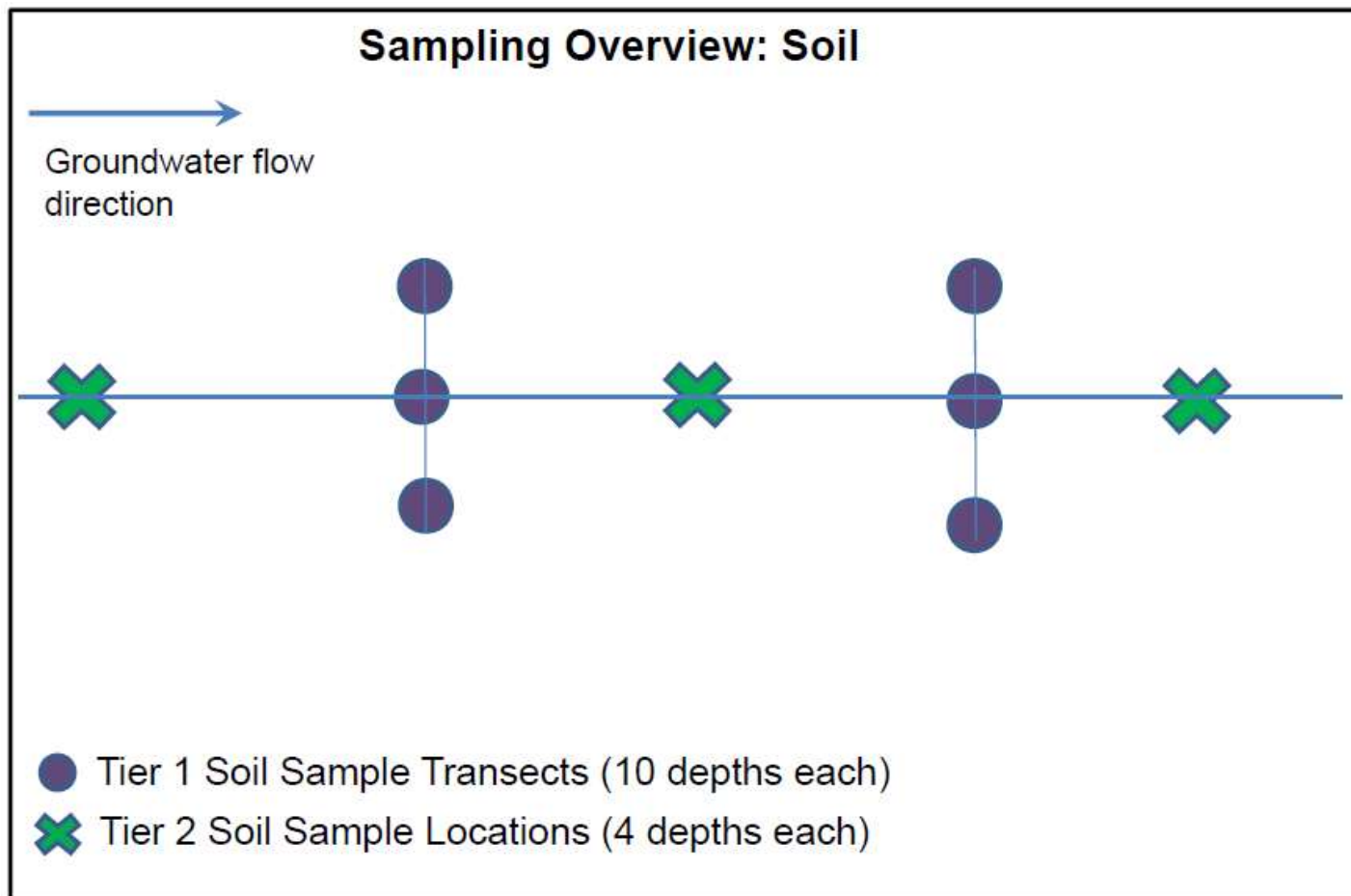
Groundwater sampling co-located; 4 samples per point

2018 ER Training – March 6-8, 2018

PFAS Characterization at NAS Jacksonville FFTF

LOCATION 3

Stratigraphy through Cross Section

LOCATION 14

Boring Log

Estimated K (from HPT)

KEY POINTS:

- Big differences in low-k zones between locations
- Shallow low-k layer near source is very thin
- Deeper clay units suspected (starting at 30 to 50 ft bgs?)

A (Near Source) ⟶ **A'** (Downgradient)
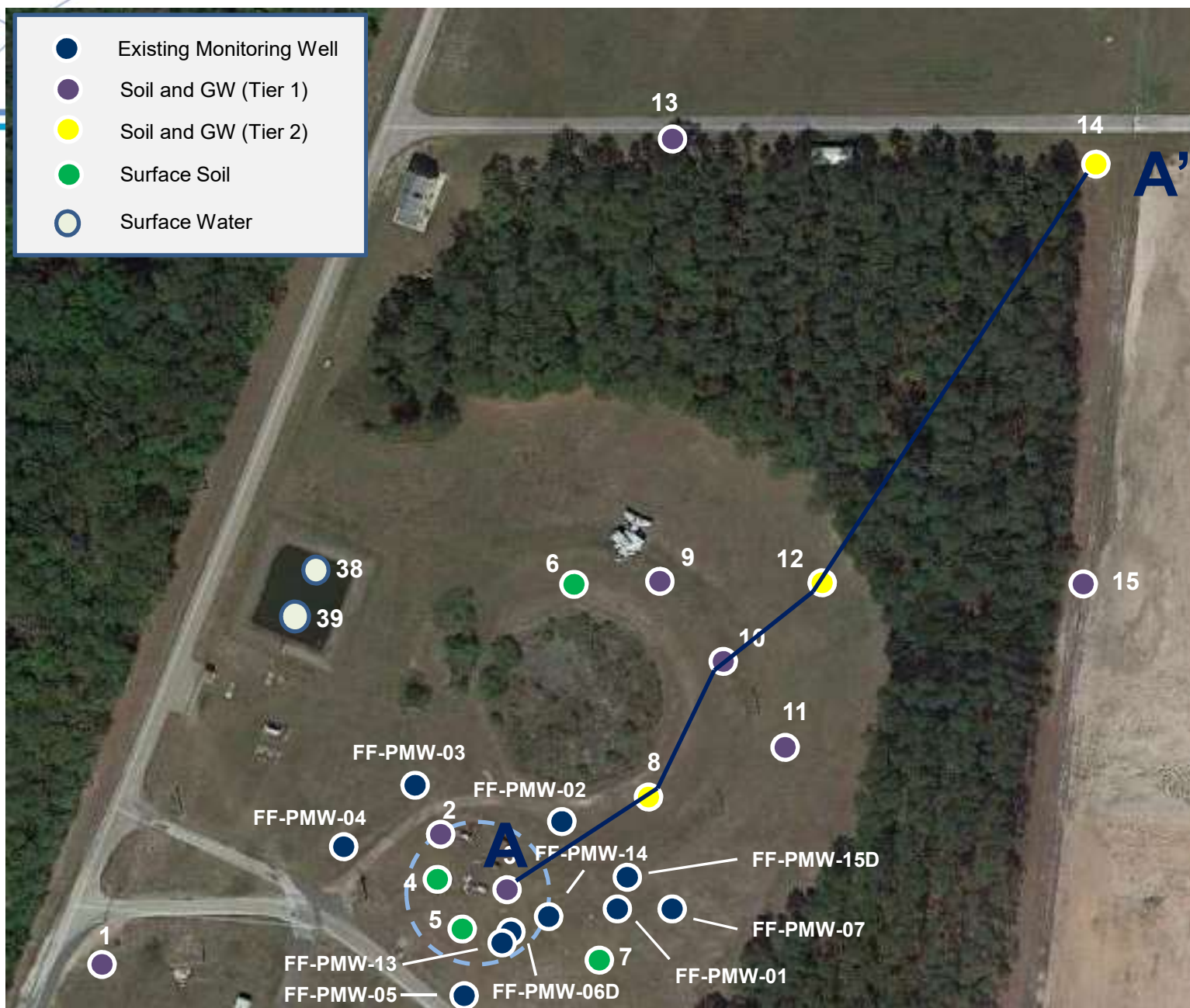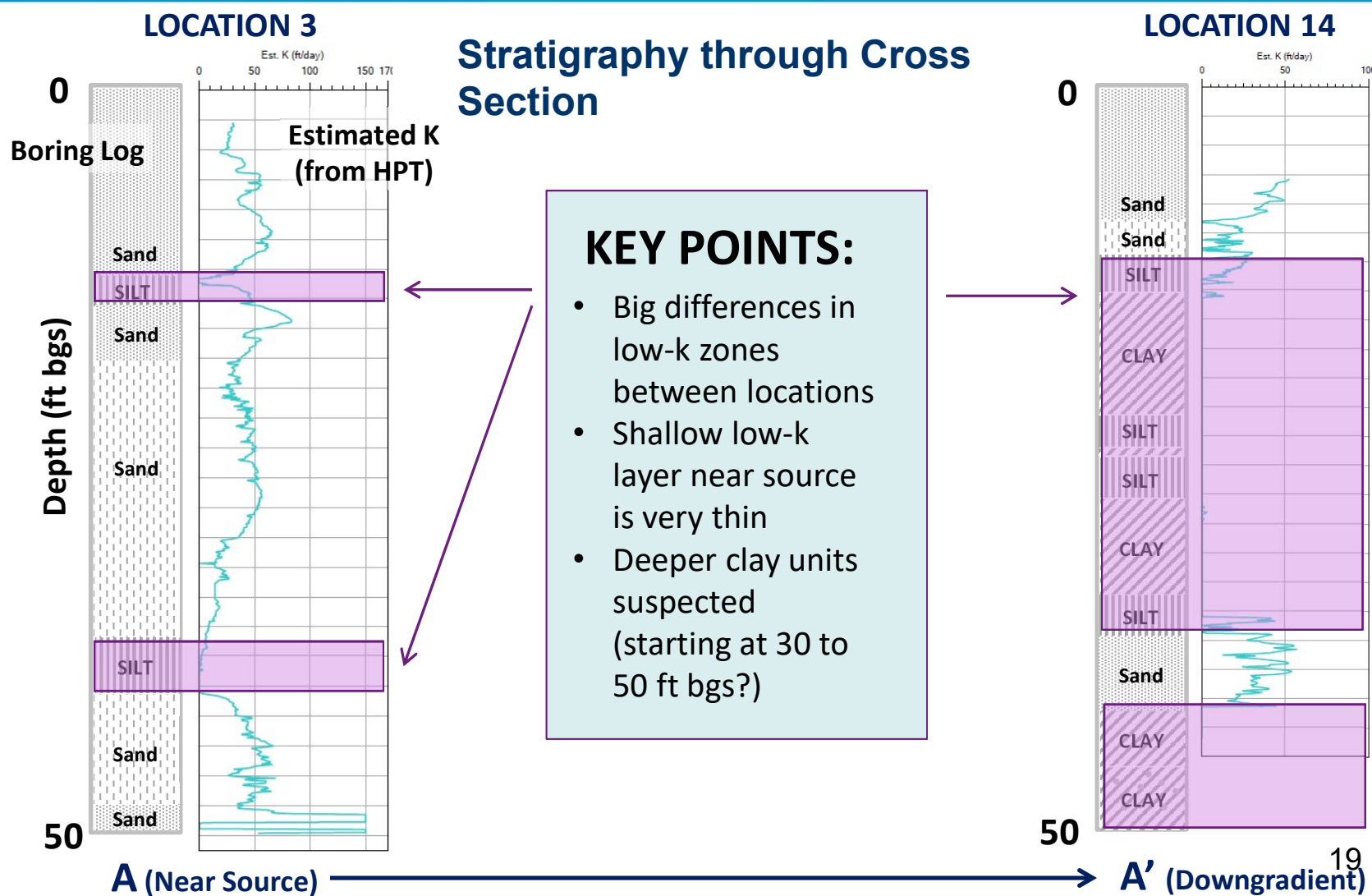
PFAS Characterization at NAS Jacksonville FFTF
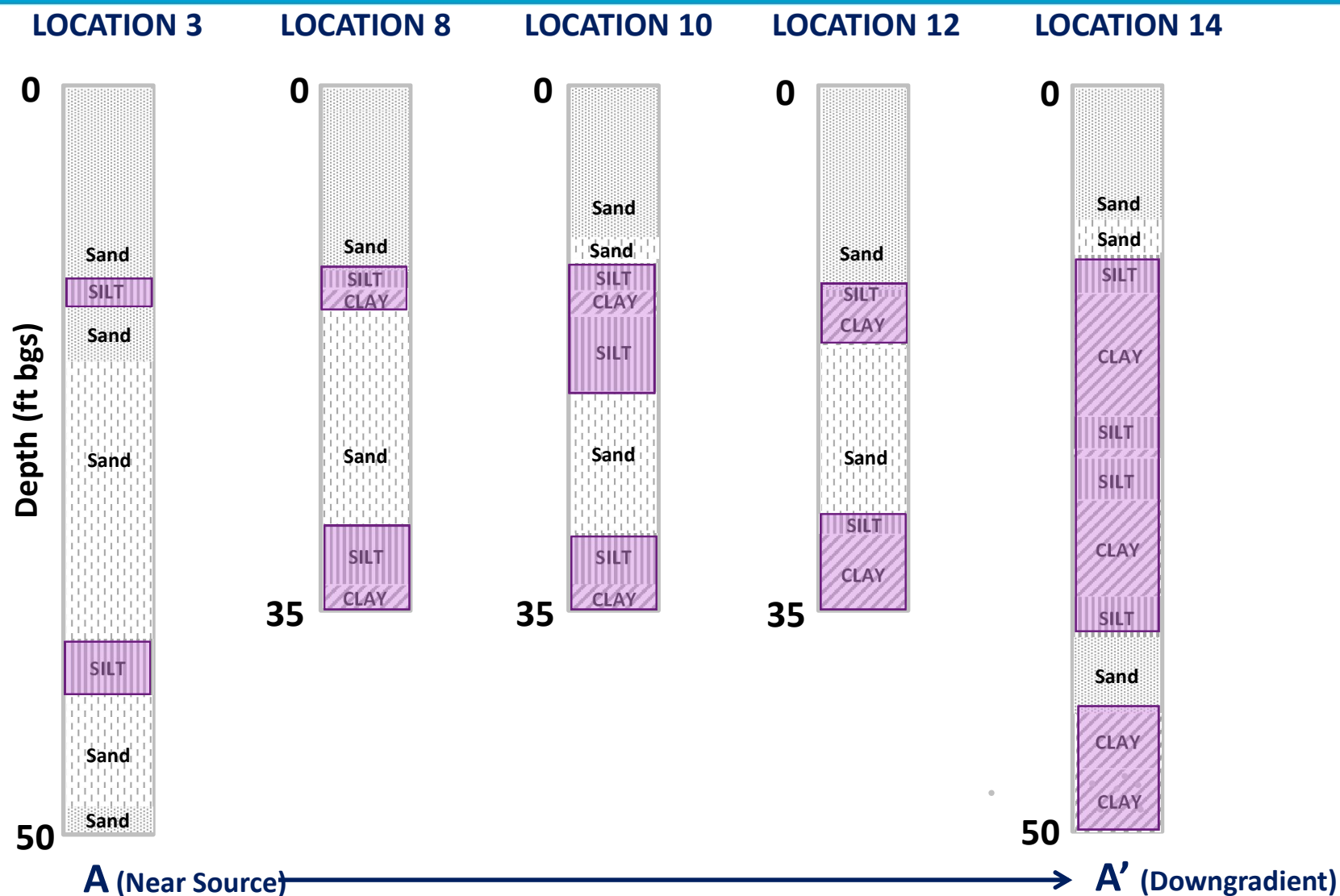
PFAS Characterization – PIGE Screening for PFAS by Fluorine Determination

- University of Notre Dame: Screening of Total Fluorine by Particle-Induced Gamma ray Emission spectroscopy (PIGE)

- Extraction of water onto solid phase "pellet", then thin-sliced, shot with beam
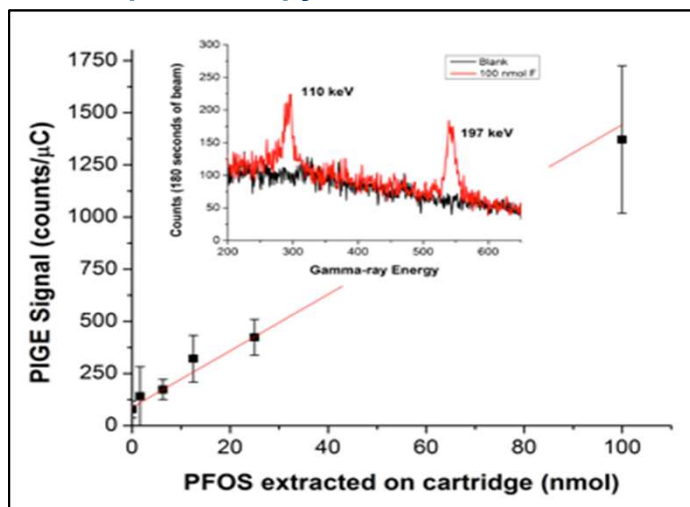
- Can also assay solids directly

- PIGE signal corresponds to total organofluorine
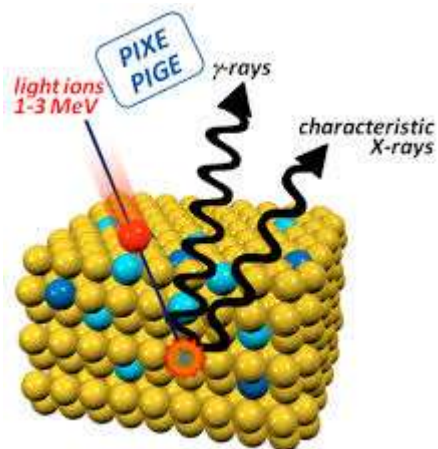
PIGE Spectroscopy of PFOS in Water

PFAS Characterization – PIGE Screening for PFAS by Fluorine Determination

PIGE Screening Data:

Groundwater (range of ppb F from multiple sample depths)

Legend:
- ● Existing Monitoring Well
- ● Soil and GW (Tier 1)
- ● Soil and GW (Tier 2)
- ● Surface Soil
- ○ Surface Water

100 ppb based on PIGE

18-43
17-
39-191
70-151
26-44
24-216
53-642
73-146
18-26
79-83
56-382
18-23
83-899
29-48 *
640-642
28-70
33-132
44-57 *
34-84
609-1336
12-146

PFAS Characterization – PIGE Screening for PFAS by Fluorine Determination (ppb F)
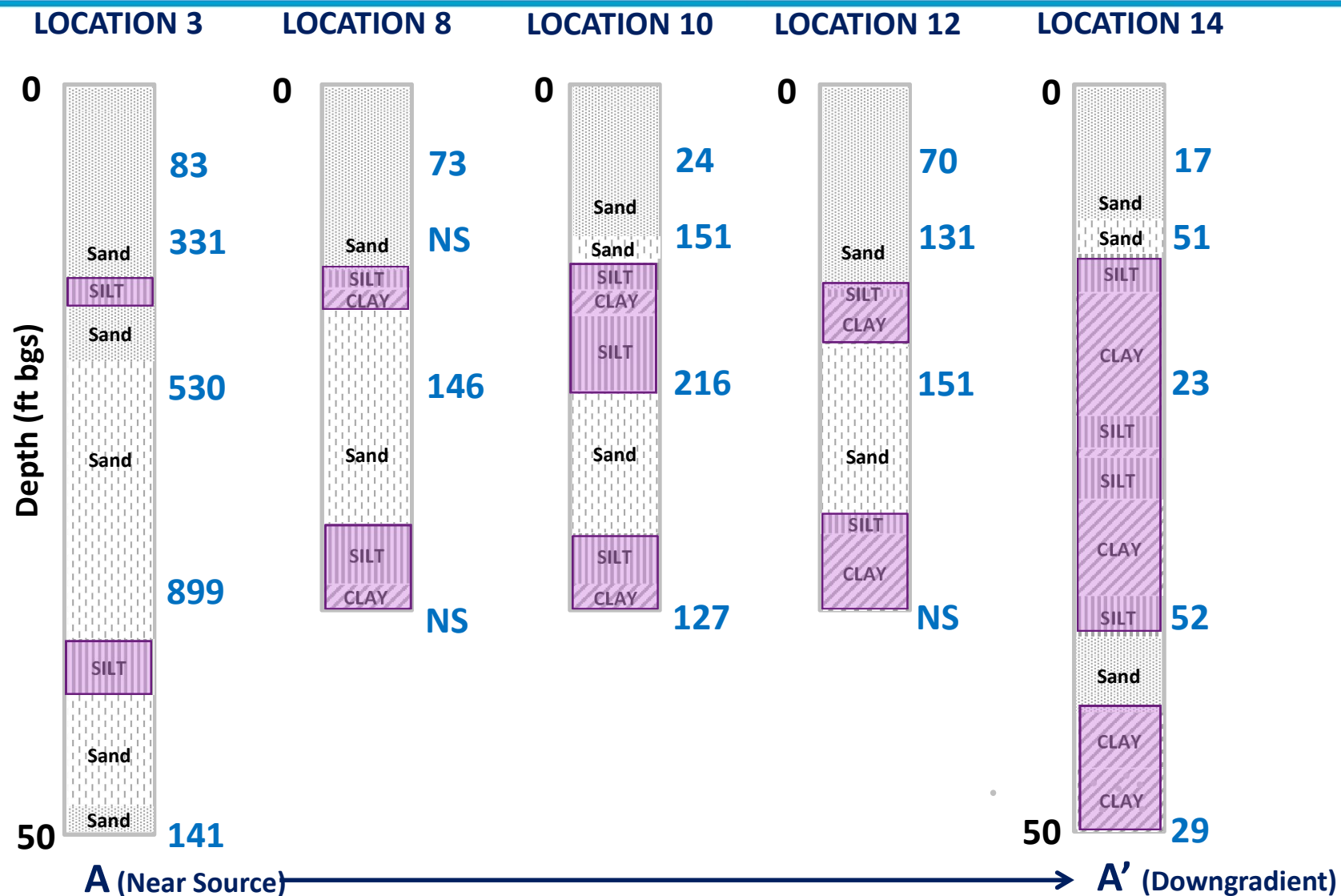
PFAS Characterization – PIGE Screening for PFAS by Fluorine Determination (ppb F)

SHALLOW EXISTING MONITORING WELLS

Depth (ft bgs)

0

Sand

SILT

15

Interface (mean of 8 wells) = **36**

Mid-Screen (mean of 8 wells) = **68**
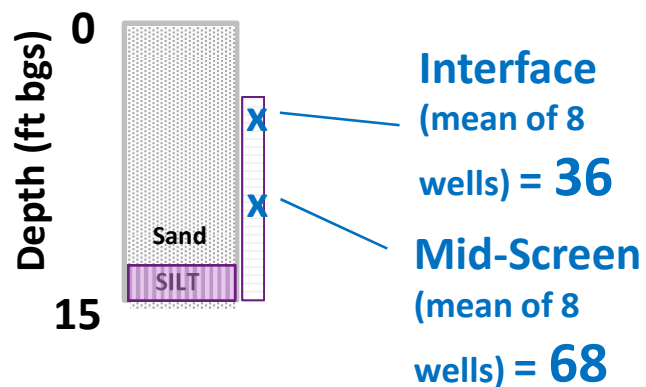
DEEPER EXISTING MONITORING WELLS

0

Sand

SILT

Sand

Sand

35

Interface (mean of 2 wells) = **625**

Mid-Screen (mean of 2 wells) = **989**
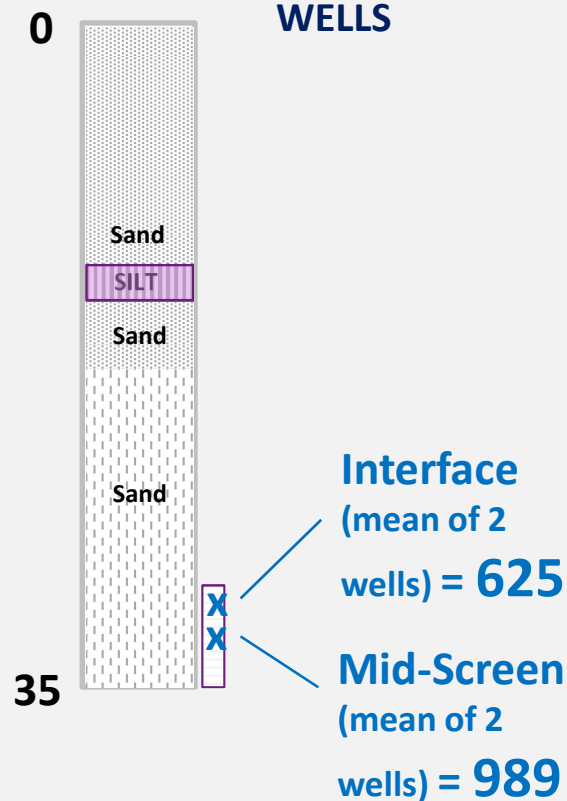
Note: All existing monitoring wells installed near source (Fire Training Pit)

PFAS Characterization – PIGE Comparison with LC-MS/MS

Total PFAS:

Surface Soil (ng/g)

– Comparison with

PIGE data

PFAS Characterization – PFAS in Soil by LC-MS/MS Using High Resolution MS Library

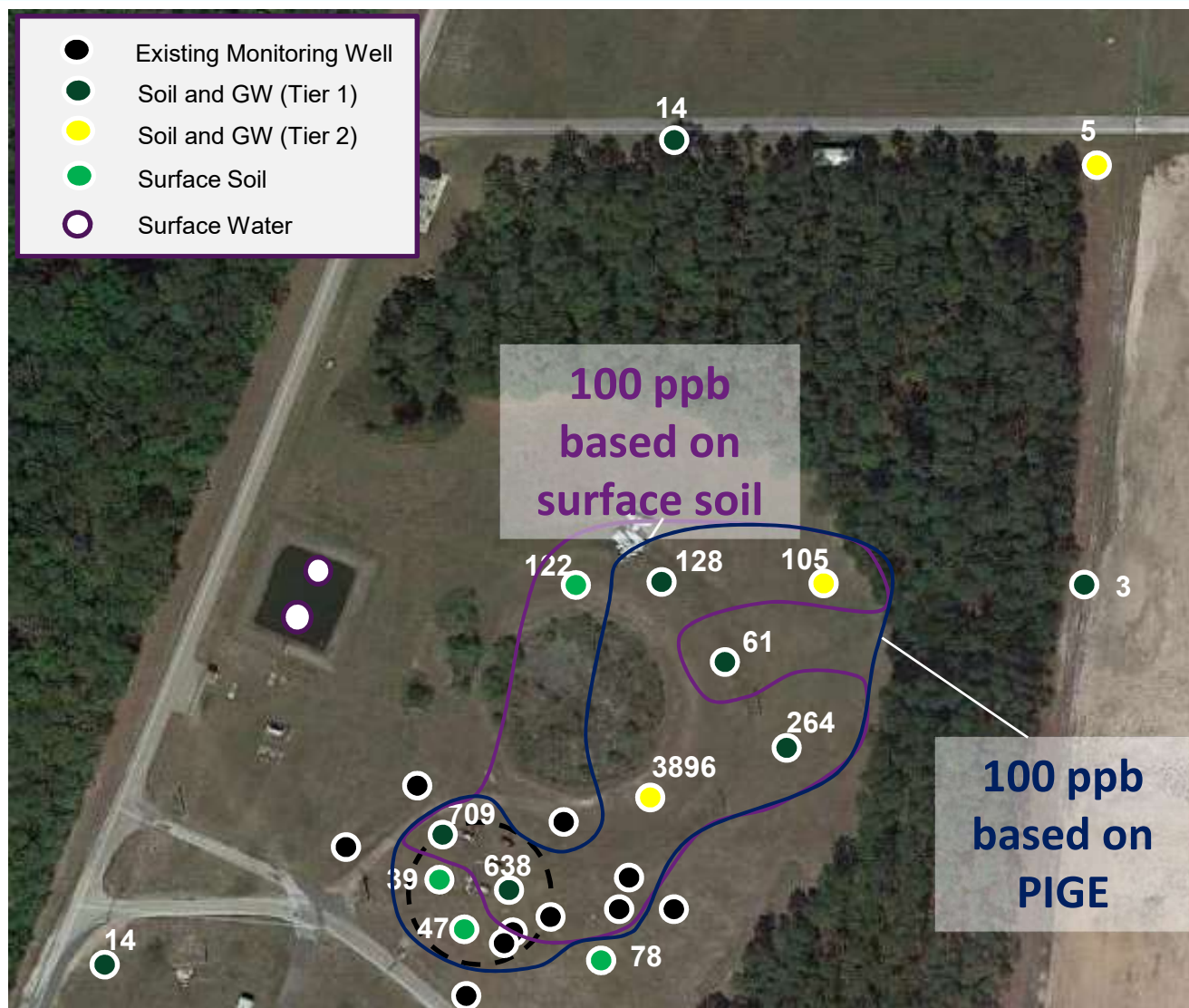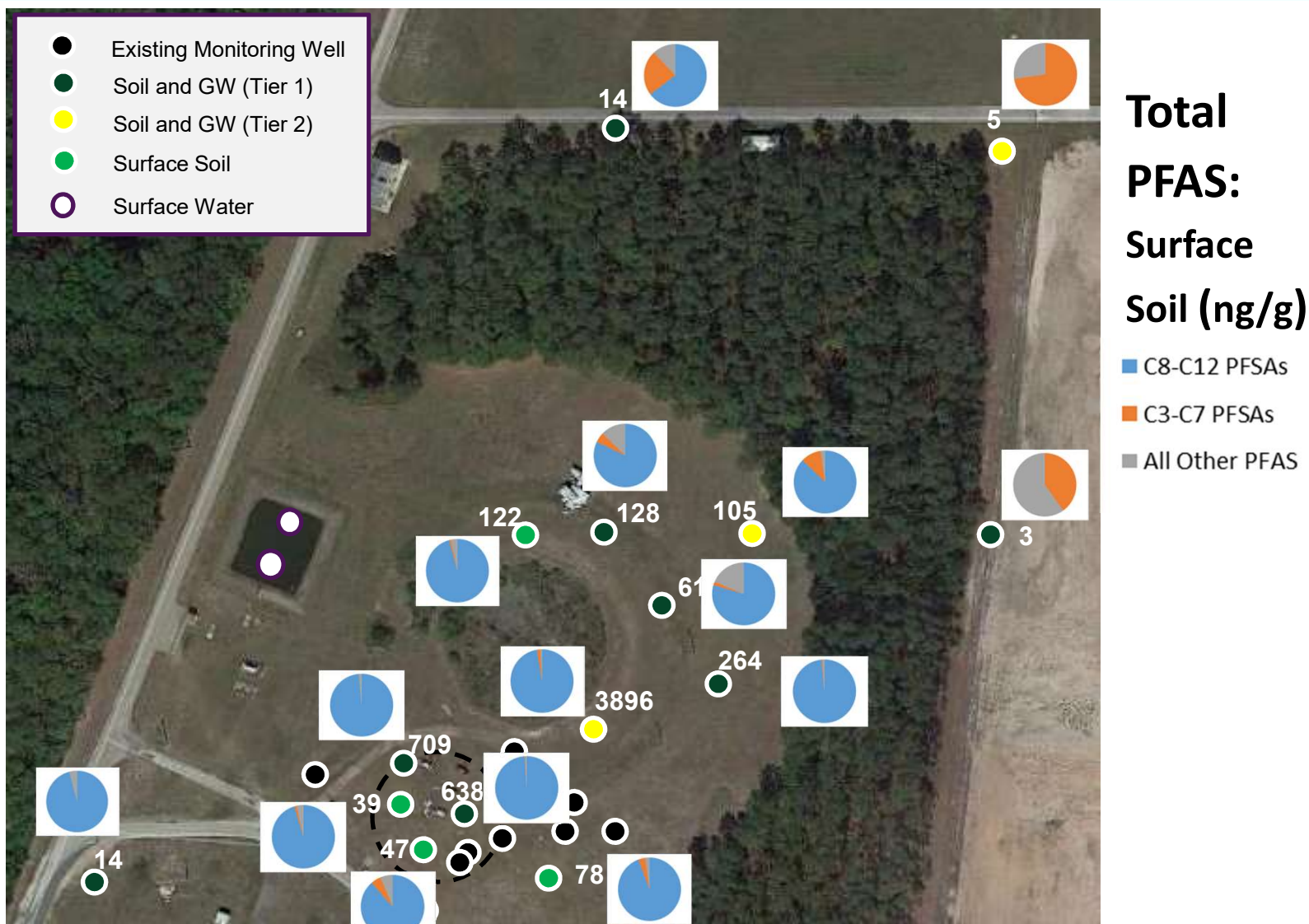# PFAS Characterization – PFAS in Soil by LC-MS/MS Using High Resolution MS Library
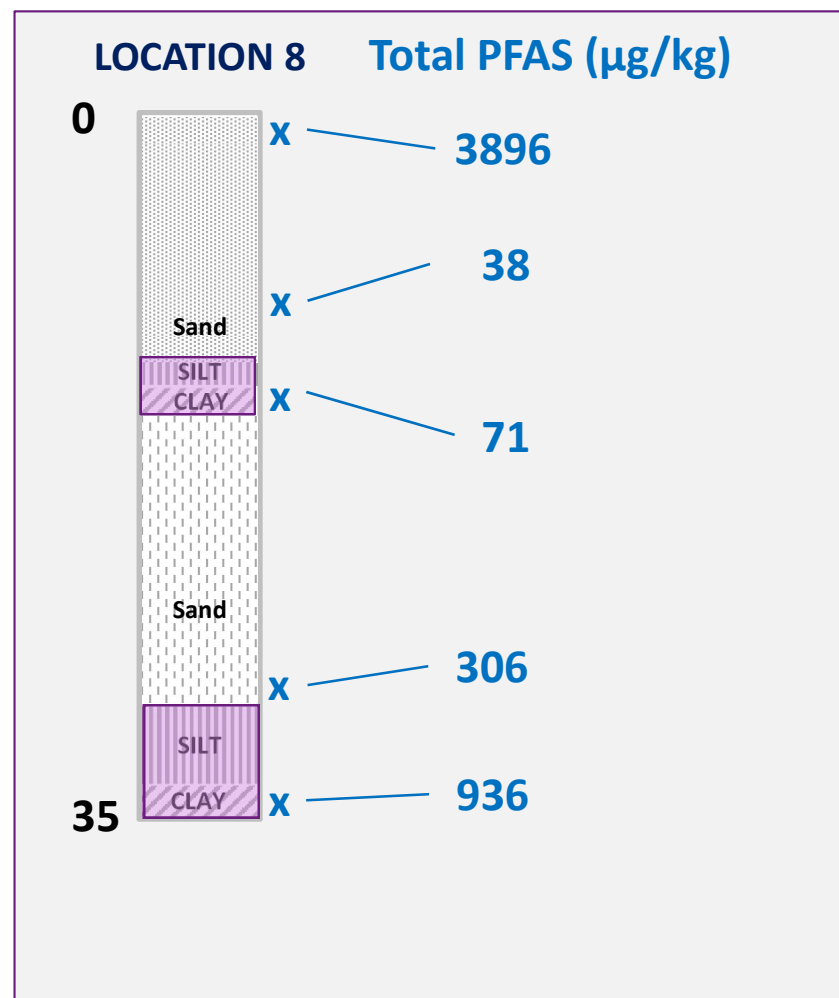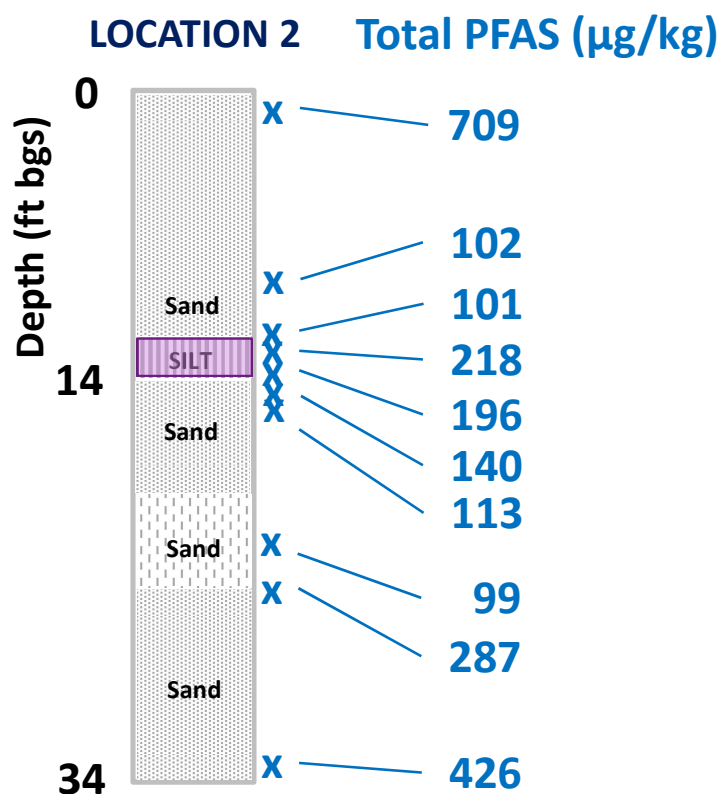
LOCATION 2   Total PFAS (µg/kg)

Depth (ft bgs)

0 — X — 709

Sand

102
101
SILT — 218
14
Sand — 196
140
113

Sand — X
Sand — X — 99
287

Sand

34 — X — 426

LOCATION 8   Total PFAS (µg/kg)

0 — X — 3896

Sand — X — 38

SILT
CLAY — X — 71

Sand

X — 306

SILT
CLAY — X — 936

35

Note: Both borings located near source (Fire Training Pit)

PFAS Characterization – PFAS in Soil by LC-MS/MS Using High Resolution MS Library

Note: Both borings located near source (Fire Training Pit)

Legend:
- C8-C12 PFSAs
- C3-C7 PFSAs
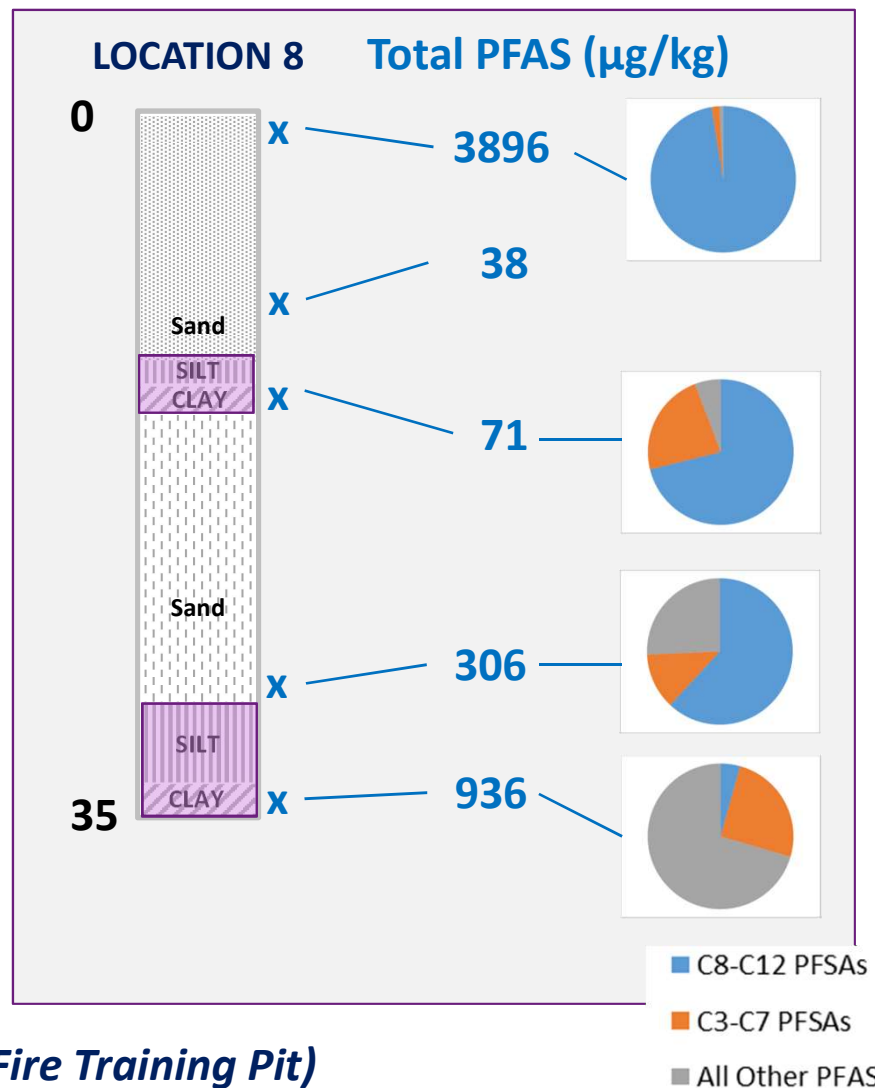- All Other PFAS

PFAS Characterization – PFAS in Soil by LC-MS/MS Using High Resolution MS Library

LOCATION 2 — Total FTSA (µg/kg)

Depth (ft bgs): 0, Sand, SILT, 14, Sand, Sand, Sand, Sand, 34

Values: 8, 5, 5, 5, 14, 13, 10, 28, 24, 45

4:2, 6:2 FTSA
8:2+ FTS

LOCATION 8 — Total FTSA (µg/kg)

Depth (ft bgs): 0, Sand, SILT CLAY, Sand, SILT CLAY, 35

Values: 2, 0.4, 1, 35, 53

4:2, 6:2 FTS
8:2+ FTS
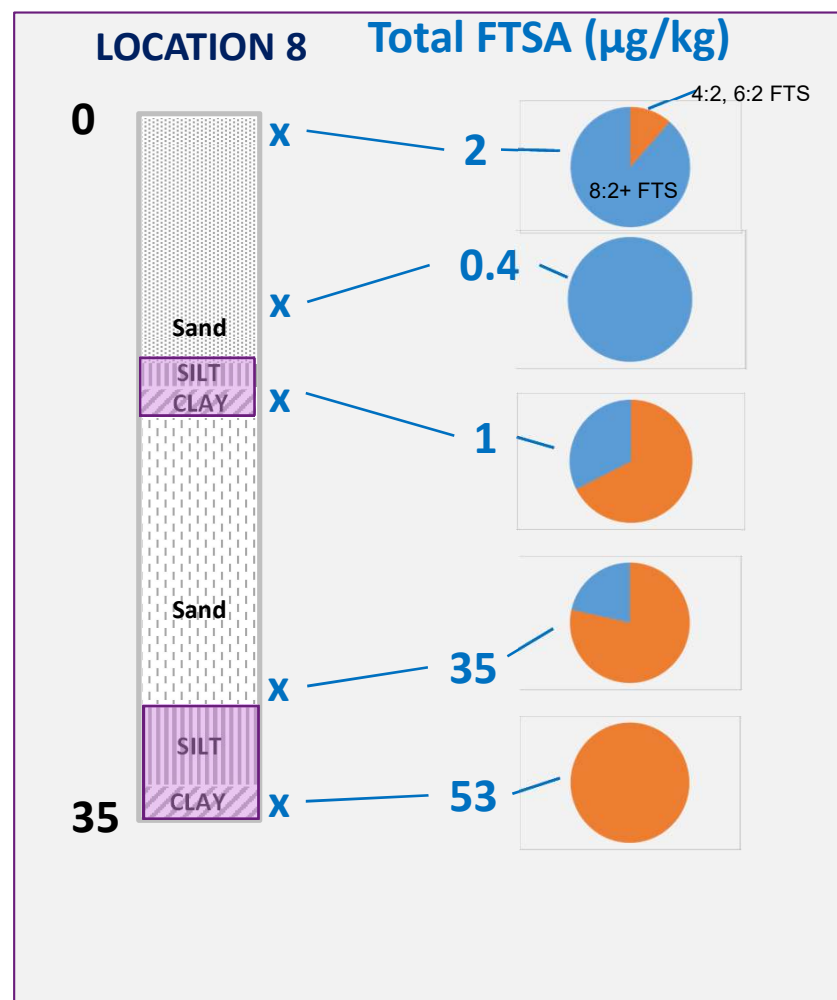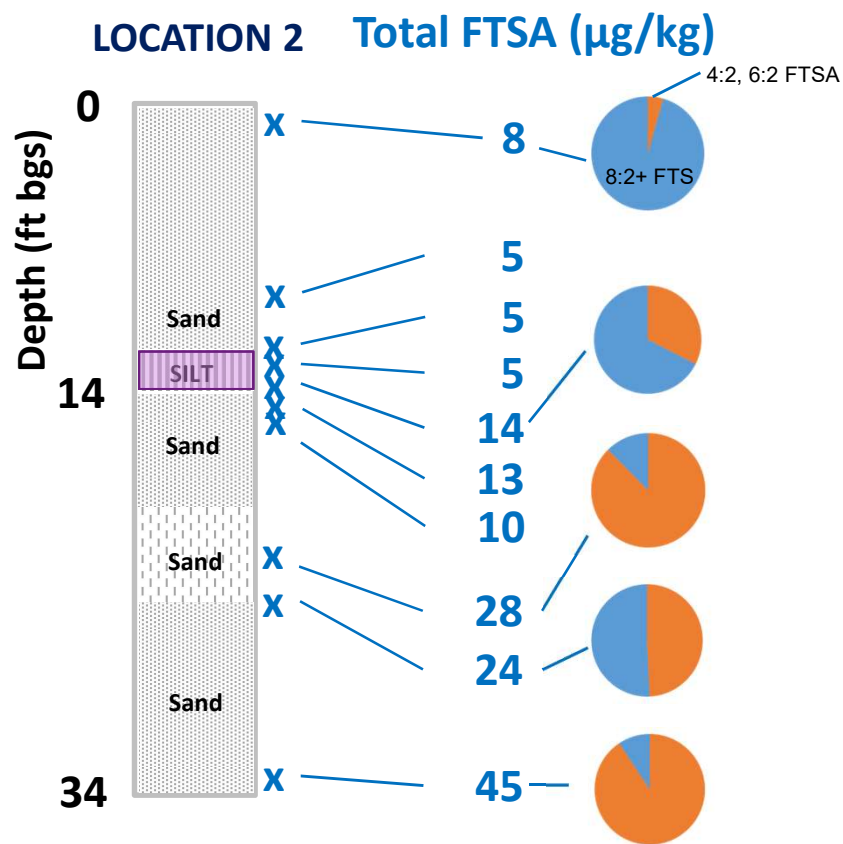
Note: Both borings located near source (Fire Training Pit)

PFAS Characterization – PFAS in Groundwater by LC-MS/MS
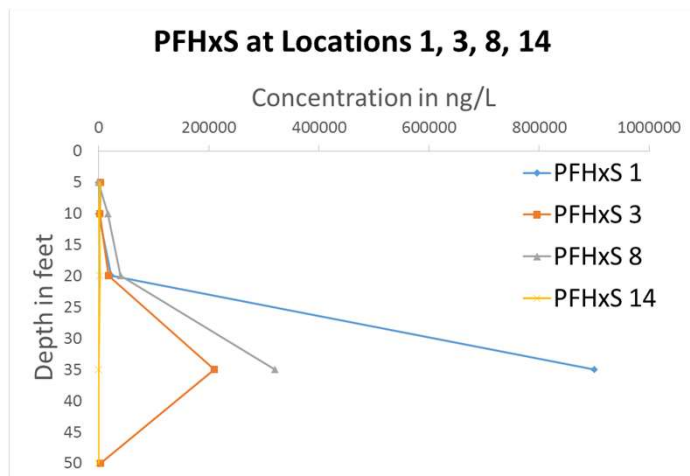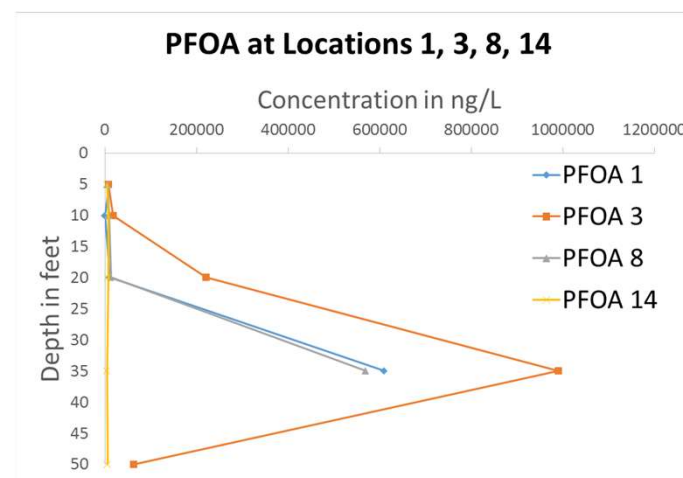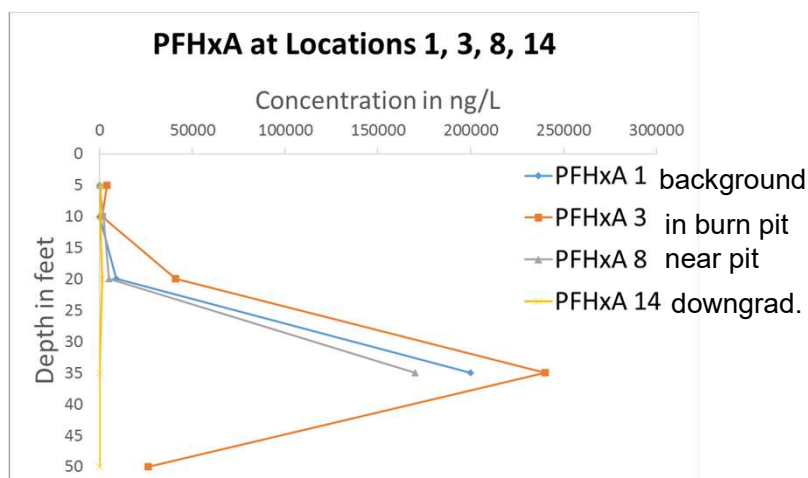
PFNA and PFDA at quantifiable levels at Location 1, 20-33 ft., suggests separate source
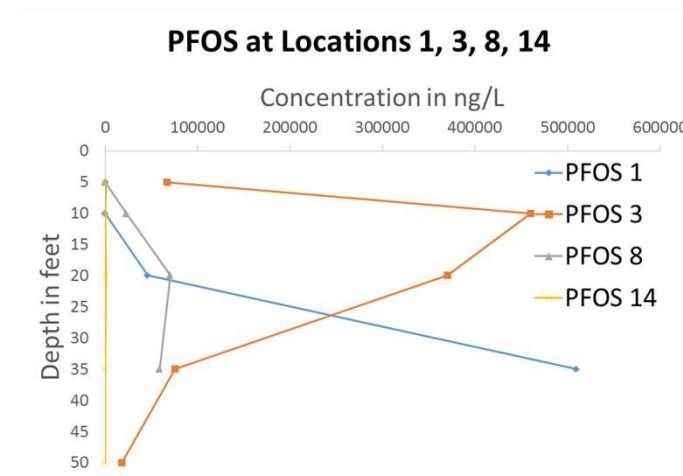
PFAS Characterization – Key Points

- Results from 1st site (JAX) suggest:
    - PIGE a good screen for relative PFAS concentrations
    - Low-k zones represent PFAS sink/back diffusion zone
    - PFSAs (mainly PFOS) highest in surface soil at source
    - Vertical gradient in groundwater evident at source; total PFAS increase with depth
        - Shorter chain proportions increase with depth in soil and water
    - Horizontal migration appears greatest for PFCAs
    - Radial transport from burn pit and multiple sources likely contribute to groundwater "background"
    - Further downgradient and background characterization ongoing

PFAS Treatment Using Thermally-Enhanced *in situ* Persulfate Oxidation Under Acidic Conditions with P&T (ESTCP ER-201729)

- *In situ* persulfate oxidation for PFAS mineralization
- Effective in the lab under acidic conditions for oxidizing PFCAs and PFAA precursors
  - ◆ Fully effective for PFAS remediation at sites that only used fluorotelomer-based AFFF
  - ◆ Enhances PFAS destruction and mass removal, markedly decreasing duration and cost of remediation
- Demonstration at a DoD site using site-specific design optimized by lab tests

Dr. John Kornuc, NAVFAC EXWC
Dr. David Sedlak, University of California at Berkeley
Dr. Rula A. Deeb, Geosyntec Consultants
Bruce Marvin, Geosyntec Consultants
Elisabeth Hawley, Geosyntec Consultants

PFAS Treatment Using Thermally-Enhanced Persulfate Oxidation Under Acidified Conditions and P&T

PFAAs are mineralized and F mass balance is accounted for

Conditions

$[S_2O_8^{2-}]_0 = 50$ mM
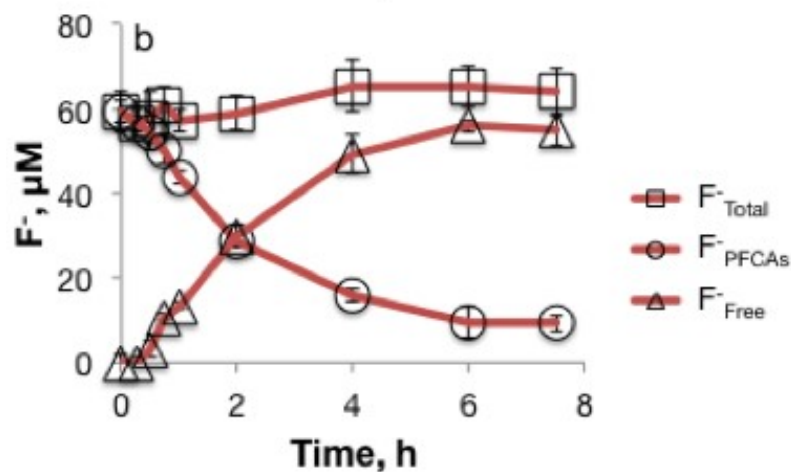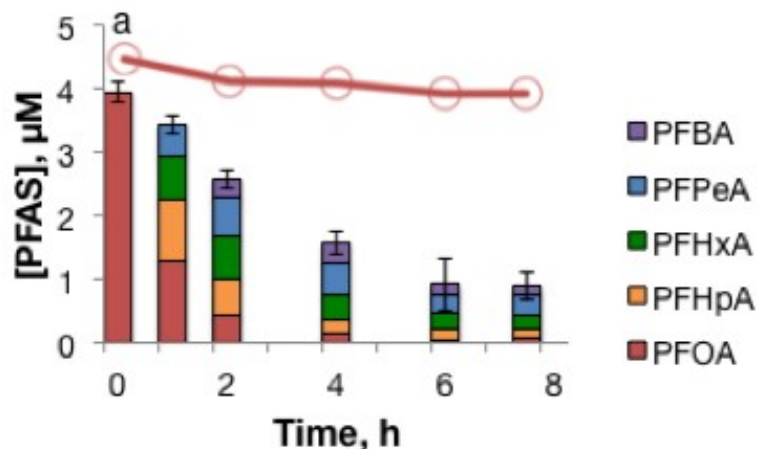
$T = 60\text{-}85^\circ$ C

pH 2.5-3.0

Technology works in the presence of sediments and groundwater constituents

Conditions

$[S_2O_8^{2-}]_0 = 50$ mM

200 g/L sediments

$T = 60\text{-}85^\circ C$

pH 2.5-3.0

Technology mineralizes PFAAs in telomer-based AFFF (Ansul AFFF)

Conditions

$[S_2O_8^{2-}]_0 = 50$ mM

$T = 60-85^\circ$ C

pH 2.5-3.0

Lodyne (6:2 FtTAoS)
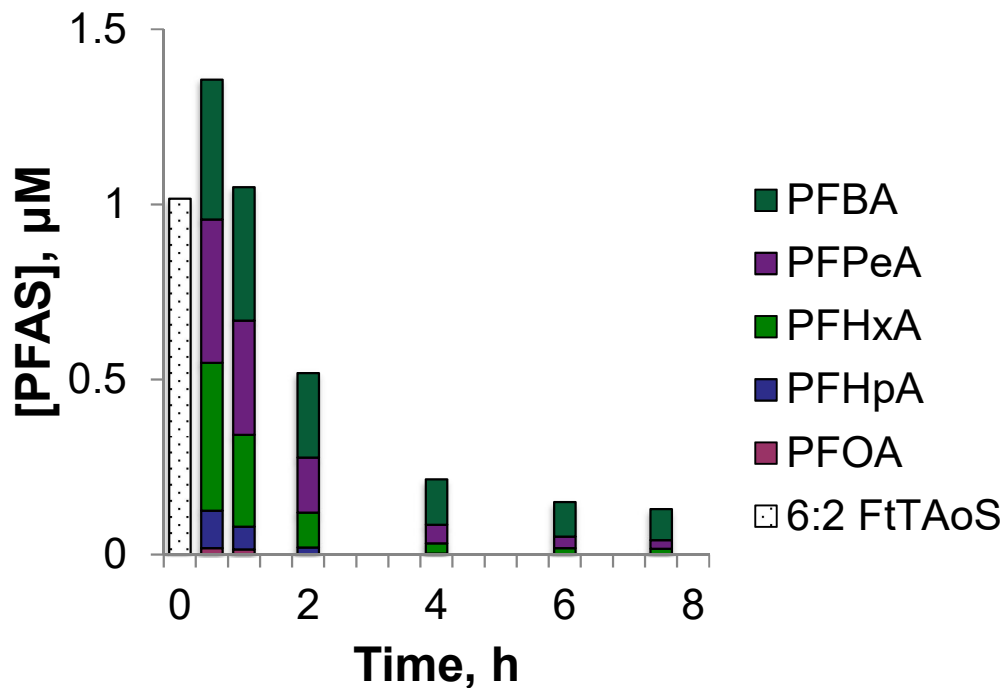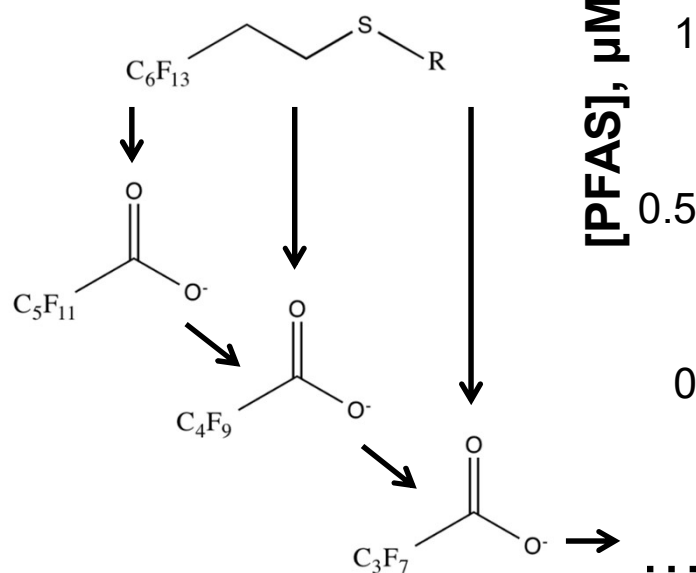
Note: *Funding provided by NIEHS Superfund Center. See Bruton, 2016 for details.*

PFAS Treatment Using Thermally-Enhanced Persulfate Oxidation Under Acidified Conditions and P&T

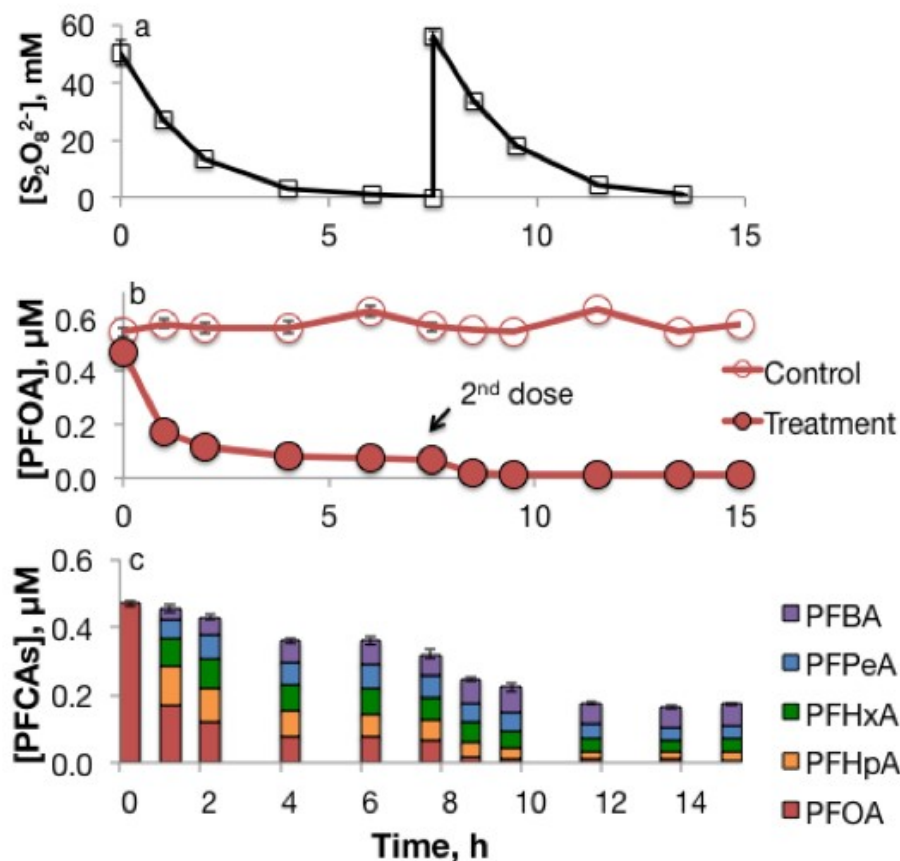*Technology is unable to remove PFOS from 3M AFFF which is consistent with <u>all</u> chemical treatments to date*

Conditions

$[S_2O_8^{2-}]_0 = 50$ mM

$T = 60-85^\circ$ C

pH 2.5-3.0
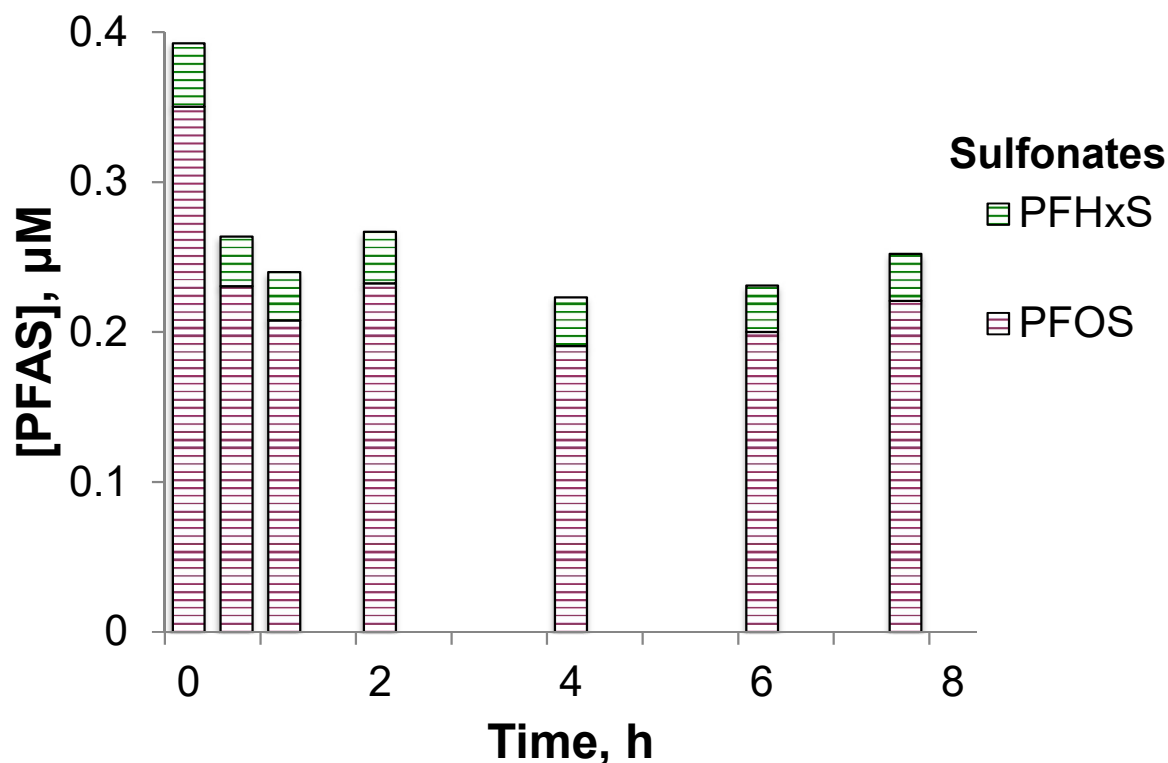
Note: Funding provided by NIEHS Superfund Center. See Bruton, 2016 for details.

Treatment of PFAS by Activated Persulfate under Thermally Enhanced and Acidified Conditions

Laboratory treatability tests and modeling

- Conduct groundwater batch studies
  - ♦ Baseline laboratory characterization
  - ♦ Assess PFAS transformation by heat-activated persulfate

- Conduct groundwater/soil slurry batch studies
  - ♦ Validate feasibility and effectiveness of peroxide heating
  - ♦ Evaluate effect of persulfate addition on aquifer pH, aquifer buffering capacity and metals dissolution
  - ♦ Assess oxidant demand and estimate PFAS degradation rates
  - ♦ Assess conditions for neutralizing acidified groundwater and the effect of neutralization to stabilize dissolved metals

- Conduct simple 3D modeling to evaluate heat flow and oxidant distribution

Overview of field demonstration
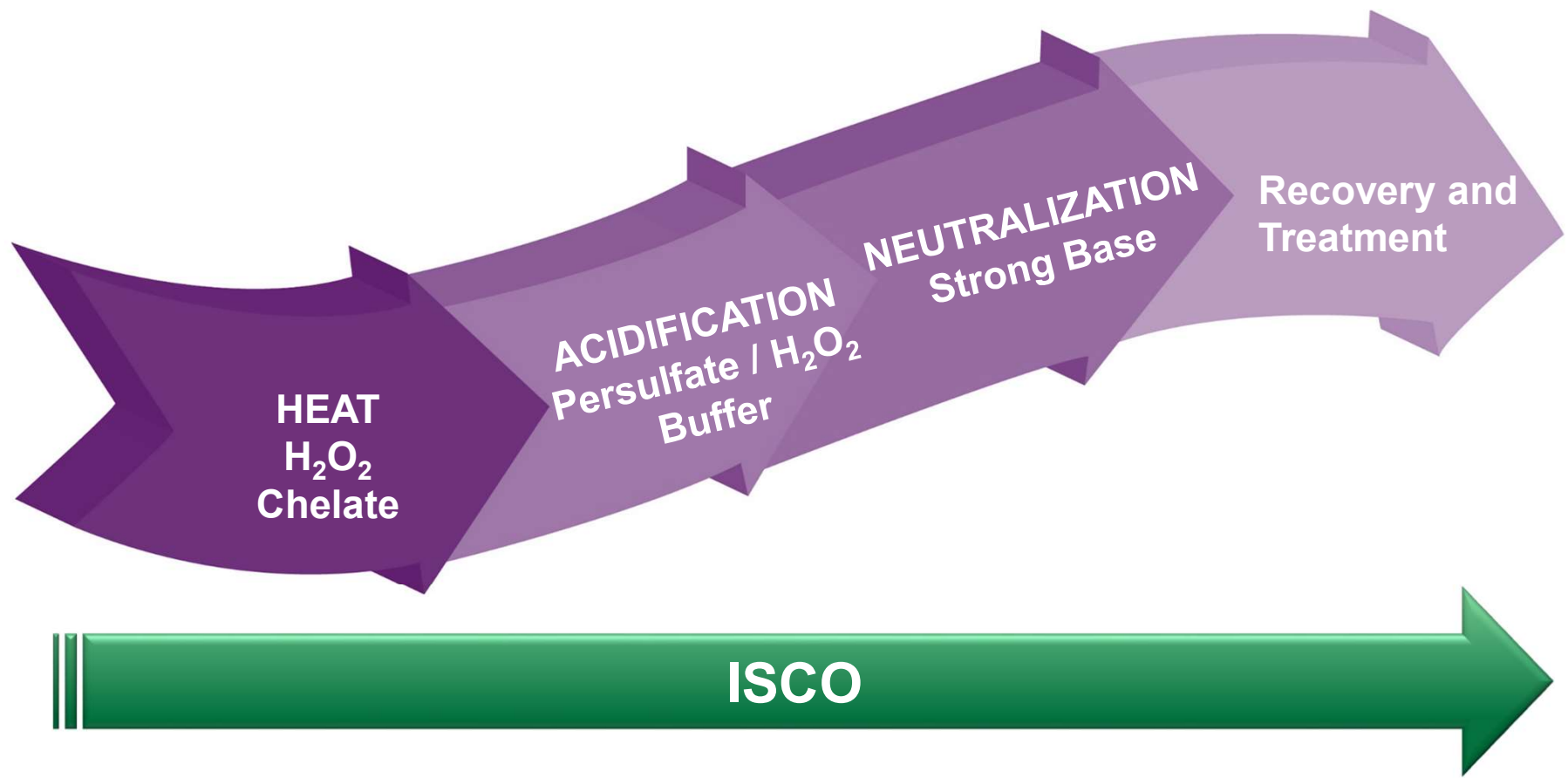
Treatment of PFAS by Activated Persulfate under Thermally Enhanced and Acidified Conditions

Field demonstration layout

- Circulation between injection and extraction wells
- Monitor pH and temperature throughout treatment area
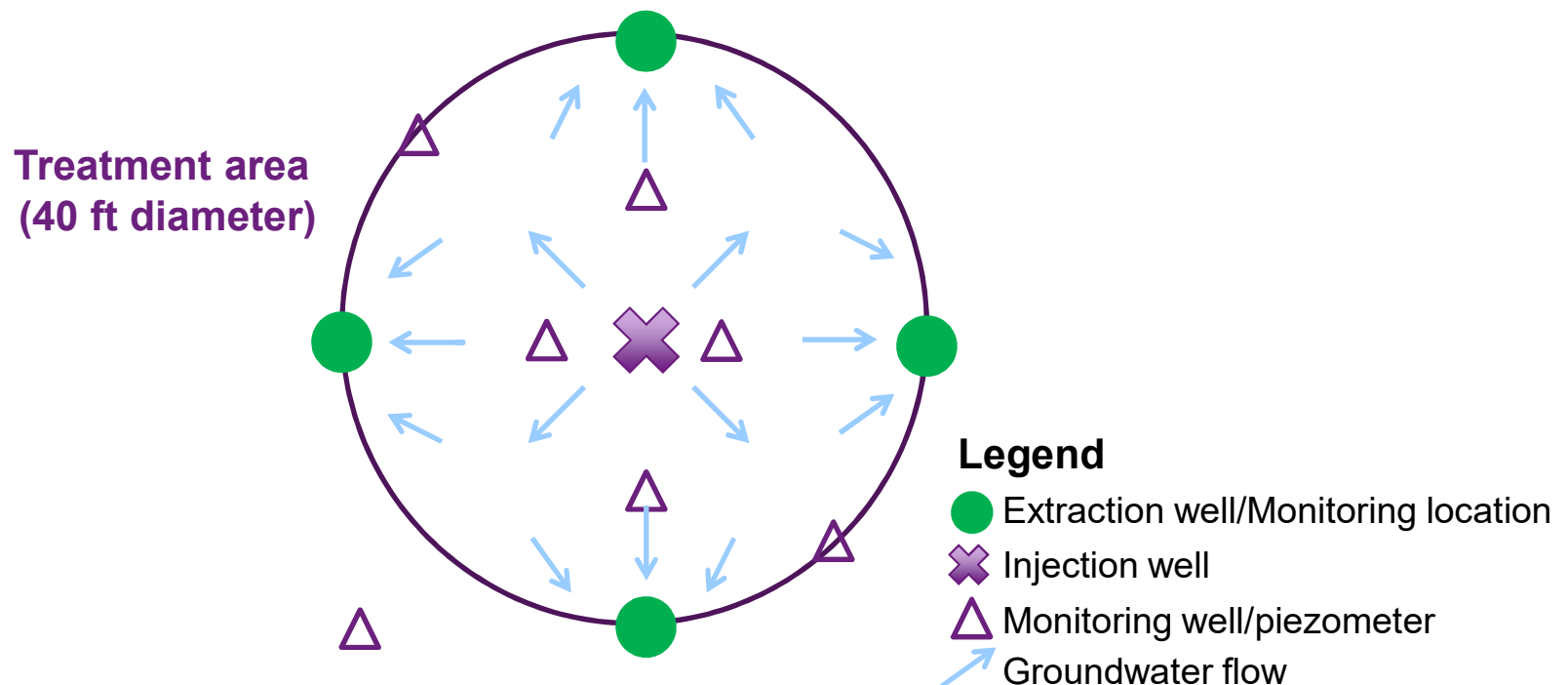
Treatment area
(40 ft diameter)

Legend
- ● Extraction well/Monitoring location
- ✖ Injection well
- △ Monitoring well/piezometer
- ↗ Groundwater flow

Treatment of PFAS by Activated Persulfate under Thermally Enhanced and Acidified Conditions

Field demonstration ex situ treatment

- Treat extracted groundwater using GAC sorption
- Install piping, holding tanks, injection equipment and GAC treatment unit
  - ♦ Use pre- or post-treatment if needed to remove significant solids generated during pH/redox changes or to comply with discharge requirements

Process flow: TYP EW (4) → pH ADJUSTMENT → FILTRATION → GAC SORPTION → OXIDANT BUFFER CHELATE → FILTRATION → DISCHARGE → IW (1)

⊏⊐ Used if significant solids are generated during ex situ treatment/pH adjustment
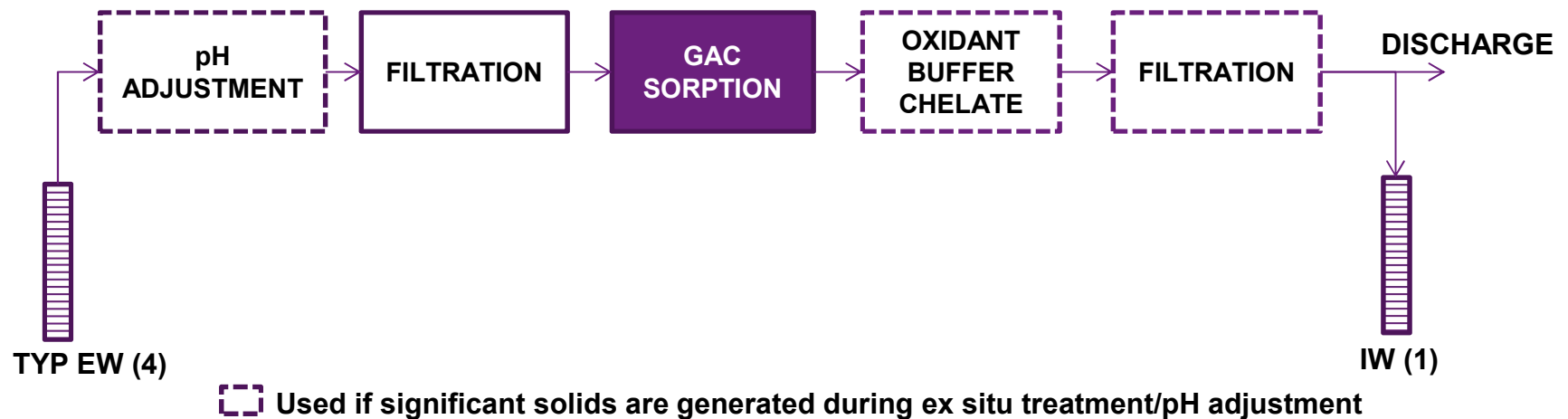
Effects of Prior Treatment of Co-contaminants on PFAS (NESDI 534)

- Prior treatment of co-contaminants (TPH, CVOCs etc)

- Reducing conditions "preserve" PFAS

- Introducing oxygen, stimulating bio, likely transforms precursors

- Fluorotelomers may transform to PFAAs, including PFOA

- Observed in groundwater discharge to surface, WWTP, HIPOX units etc.)

- May occur in prior treatment especially oxidation (ISCO, air sparging, SVE, bioremediation etc.)

- May have mobilized sorbed species

- Pump & Treat may have spread PFAS by effluent discharge (non-binding species, displacement)

John Kornuc, Ph.D., NAVFAC EXWC
Ramona Darlington, Ph.D., Battelle

Assessment of PFAS Sorbents, Stabilizers, Other Treatment, Determination of Site-Specific Leaching and Retardation Factors (NESDI 555)

Rate Determination of PFAS Transport

- Measurement of site-specific sorption coefficients
  - Used in groundwater models to determine the likelihood and extent of plume migration or attenuation

Selection of Best Available Sorbent for PFAS Treatment in Groundwater

- RPMs can request batch and column tests using site-specific groundwater samples
- PFAS:
  - Various granular activated carbons (GACs)
  - Ion Exchange Resins – effectiveness, regeneration capacity
  - Novel sorbents e.g. cross-linked cyclodextrins
  - Pre-treatment to increase binding efficiency (pH, ionic strength adjustment etc.)
  - Pre-treatment to knock down natural organic matter
  - Analysis of total PFAS to ensure that shorter-chain PFAS's (e.g. C4 carboxylates) are being sorbed

Validation of Vendor Claims

- Data and literature review of currently marketed technologies for PFAS
- Electrochemical treatment, biological/chemical oxidation, sonolysis, precipitation
- In-house tests or coordination of tests at affiliated university laboratories

Knowledge Check

1. PFAS tend to persist at sites long after they stop being used because:
   a. They do not degrade easily
   b. They diffuse into low-k zones and slowly back-diffuse
   c. They sorb to the organic fraction of soils
   d. All of the above

2. Which PFAS would you expect to find at the leading edge of a plume:
   a. Those with a longer carbon chain length
   b. C4 Carboxylate
   c. Fluorotelomers
   d. All of the above

3. Previous ISCO treatment at a PFAS site likely:
   a. Reduced perfluoroalkyl carboxylate concentrations
   b. Did nothing to PFAS since they are not degradable
   c. Transformed precursors to perfluoroalkyl carboxylates like PFOA

PFASs Transport Key Concepts

Source Zone

Composition: Largely cationic/Zwitterionic PFAS
Typical PFAS: Precursors, PFOS-Based: PFOS, PFHxS, PFBS; Telomer-Based: 6:2 FtS, 8:2 FtS, 4:2 FtS;
Key Processes: Fine grained soils have reservoir of long-chained Cationic/Zwitterionics PFAS due to:
- Polar sorption (important process)
- Non-polar sorption (likely less important than polar sorption)
- Matrix diffusion (unknown importance)
- Biodegradation near surface from oxygen influx (speculative)

Relative Transport Velocity: Slow due to matrix diffusion, high sorption

Mid-Plume Zone

Composition: Anionic PFAA precursors
Key Processes:
- Advection in transmissive zones,
- Relatively little sorption
- Relatively little biodegradation due to anaerobic conditions
- Some matrix diffusion

Relative Transport Velocity: Fast

Downgradient Plume Zone

Composition: Significant PFAAs
Typical PFAS: Shorter-Chain PFAS: PFEtS, PFPrS
Key Processes:
- Advection in transmissive zones,
- Biodegradation generates short chained PFAAs
- Low sorption means high mobility of short chain PFAAs

Relative Transport Velocity: Fast

Brady, 2017

Non-polar sorption Polar sorption
Soil organic
$F_n-X-SO_3^-$ F_n-X-NH^+
$F_n-X-COO^-$ $F_n-X-COO-Ca^+$ cation bridging
F_n-X-NH^+ Clay
Modes of PFAS sorption

PFAS Sources

Example: Aerobic biotransformation pathway 8:2 FTOH (Buck et al., 2014; adapted from Wang 2009

LNAPL

Hydrocarbon + PFAS Plume

Mobile Precursors

PFAS Plume

C8   *C7*   *C6*   *C5*   *C4*

Representative fluorinated carbon chain length of anionic dead end daughter products generated via aerobic biodegradation

Groundwater Flow Direction

Anaerobic   Transition   Aerobic